Europäisches Patentamt

(19) European Patent Office

Office européen des brevets

(11) EP 1 204 003 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
08.05.2002 Bulletin 2002/19

(51) Int Cl.7: **G03F 7/30, G03F 7/32**

(21) Application number: 00123444.2

(22) Date of filing: 03.11.2000

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE TR
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: **Kodak Polychrome Graphics Company Ltd.**
Norwalk, Connecticut 06851 (US)

(72) Inventors:
• **Timpe, Hans-Joachim, Prof. Dr.**
  37520 Osterode (DE)
• **Fiebag, Ulrich**
  31688 Nienstädt (DE)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

(54) Process for developing exposed radiation-sensitive printing plate precursors

(57) A process for developing exposed radiation-sensitive printing plate precursors is disclosed for plate/developer systems where the electrical conductivity of the developer does not decrease to the same extend as the activity of the developer decreases or even increases.

EP 1 204 003 A1

Description

[0001]   This invention relates to a process for developing imagewise exposed radiation-sensitive devices; in particular it relates to a process for developing exposed radiation-sensitive devices where the efficiency of the partially exhausted alkaline developer is lower than it appears from the measured electrical conductivity. Furthermore, the invention relates to a method for the production of a replenisher composition useful for refreshing a partially exhausted alkaline developer as well as a composition useful as a replenisher for partially exhausted alkaline developers having a lower efficiency than it appears from the measured electrical conductivity.

[0002]   The art of lithographic printing is based upon the immiscibility of oil and water, in which oily material or ink is preferentially retained by the image areas and the water or fountain solution is preferentially retained by the non-image areas of the printing plate. When a suitably prepared surface is moistened with water and an ink is applied, the background or non-image areas retain the water and repel the ink while the image areas accept the ink and repel the water. The ink on the image areas is then transferred to the surface of a material upon which the image is to be reproduced, such as paper, cloth and plastics. Commonly, the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is to be reproduced.

[0003]   Lithographic printing plates can be either negative-working or positive-working, and comprise one or more radiation-sensitive layers on a suitable substrate, such as metal or polymeric support. The radiation-sensitive layer generally includes one or more radiation-sensitive components that may be dispersed in a suitable binder. Alternatively, the radiation-sensitive component can also be the binder material.

[0004]   In order to obtain a printing plate with imagewise distribution of printable areas it is necessary to remove the non-image areas of an exposed printing plate precursor. The most common method for removing the undesired areas is to contact the exposed precursor with a developer solution.

[0005]   A negative-working printing plate generally has a light sensitive layer composed of a radiation-sensitive component such as an unsaturated resin, a negative diazo resin dissolved in a polymeric binder or an initiator system together with monomers and/or oligomers on a suitable substrate. Upon exposure to light, the exposed areas are hardened, leaving non-exposed areas removable during development. Certain negative-working printing plates contain novolac resins, a cross-linking agent, and a radiation-sensitive component that produces acid on exposure. By subsequently heating the plate, only the exposed areas are cured and the unexposed areas can be removed by a developer. The exposed, hardened areas are therefore oleophilic and will accept ink while the non-exposed underlying areas of the substrate are hydrophilic.

[0006]   Many alkaline developable positive-working printing plates generally have a light sensitive layer comprising a novolac resin and a radiation-sensitive component such as an o-diazoquinone or diazonaphthoquinone compound. Upon exposure to light the radiation-sensitive component is converted to the corresponding carboxylic acid. The use of an alkaline developer will remove only the exposed areas of the radiation-sensitive layer, leaving the surface of the support. Because the surface of the support is hydrophilic, the uncovered non-image area attracts water and repels the oily ink. The image area remaining after development is oleophilic thereby repelling water and attracting the printing ink.

[0007]   Various aqueous solutions are known for use as developers. Yamasue, U.S. Pat. No. 4,259,434, describes use of a dispersion of a silicate to develop positive-working printing plates. These solutions include alkali metal silicates, in which the ratio of SiO_2 to M_2O is from 0.5 to 0.75 ("M" being the alkali metal) at 1-4% SiO_2 concentration.

[0008]   Seino, U.S. Pat. No. 4,452,880 describes silicate-containing developers in which the SiO_2 to alkali metal oxide ratios are much higher, that is between 1.6 and 2.0, and the % SiO_2 concentration is from 2 to 9%.

[0009]   Miller, U.S. Pat. No. 5,851,735, discloses an aqueous alkaline developing composition that is useful in developing either positive-working or negative-working lithographic printing plates. The composition has a pH of at least 12 and comprises an alkali metal silicate and at least 6 wt.-% of a water-soluble or water-dispersible thickener, such as glycerol.

[0010]   Toyama, GB-A-2,276,729 (DE-A-4 411 176) discloses a developer or replenisher for both positive-working and negative-working lithographic printing plates comprising an alkali metal silicate and a water-soluble ethylene oxide adduct, obtained by addition of ethylene oxide to a sugar alcohol having not less than 4 hydroxy groups. This developer is stable and shows a high developing efficiency.

[0011]   In the development of exposed printing plate precursors the problem arises that the developer is weakened by increasing m^2 of the developed plate; in the case of alkaline developers this means that the alkalinity of the developer decreases with increasing square meters of developed plates. The weakening of the developer leads to a darker or fuller image reproduction which does not meet the requirements for a standardized printing. In the case of conventional printing plates, i.e. plates which are imagewise exposed to radiation through a mask, the change of efficiency of the developer and therefore of the image reproduction can be monitored by simultaneously copying test elements. Of course this is not possible in the case of digital plates directly exposed by means of a laser without using a mask. If the developer has a measurable electrical conductivity, as it is usually the case with aqueous alkaline developers, the

users often monitor the electrical conductivity of the used developer in order to determine the efficiency of the developer. As soon as a weakening of the developer efficiency is established by means of a lower electrical conductivity the developer is refreshed by adding a fresh developer or so-called replenisher (which has a higher concentration of hydroxide ions than the developer) to the weakened developer until the electrical conductivity of the developer again reaches its original value.

[0012]   As described in EP-A-0 556 690 the electrical conductivity of a developer does not always decrease when the alkalinity decreases due to the development of plates. Depending on the kind of developer system and also on the kind of plate to be developed the electrical conductivity of the developer may be constant, may increase or decrease with increasing square meters of developed plates although the efficiency of the developer decreases in each case. According to one theory it is assumed that ingredients of the removed radiation-sensitive layer of the developed plates and/or side reactions are responsible for the production of new ions which at least partially compensate or even over-compensate the loss of electrical conductivity due to consumption of OH⁻ ions of the developer thus resulting in a measured electrical conductivity which is not as low as it would be expected due to the consumption of OH- by the developing process. Measuring the electrical conductivity does therefore not in every case allow a conclusion on the efficiency (i.e. activity) of the developer; constant values therefore do not guarantee a constant developer activity required for the desired constant developing result.

[0013]   If there is a developer system and/or plate where the activity of the developer decreases while the electrical conductivity only slightly decreases, keeps constant or even increases the addition of a highly alkaline replenisher for increasing the activity results in an increase of the electrical conductivity.

[0014]   EP-A-0 556 690 discloses a computer controlled system for refreshing the partially exhausted developer for those cases where the value of the electrical conductivity is not a measure for the activity of the developer: This system, however, in view of the printers has the disadvantage that further expenses are necessary due to the purchase of the computer controlled system.

[0015]   Therefore, there is a need for a process which does not result in the necessity of new equipment and is easy to be carried out by the printers and even unskilled workers.

[0016]   The present invention provides a simple method for the production of a replenisher composition useful for refreshing an at least partially exhausted developer having a lower activity than it appears from the electrical conductivity.

[0017]   The method comprises the steps of

(a) measuring the activity and electrical conductivity versus unit throughput of device to be processed while using the desired developer
(b) determining the amount of hydroxide ions per unit throughput necessary for achieving the original activity
(c) for the case that the electrical conductivity per unit throughput does not decrease as it should decrease due to consumption of OH⁻, determining the amount of a electrical conductivity suppressing agent necessary for keeping the electrical conductivity constant, wherein the electrical conductivity suppressing agent is water soluble, does not react with the other components of the replenisher and developer and does not react with or attack the radiation-sensitive layer of the device to be developed, and
(d) mixing water and the hydroxide ion source with the conductivity suppressing agent and optional further components.

[0018]   The present invention also provides a method for developing radiation-sensitive imagewise exposed devices by using an alkaline developer showing electrical conductivity comprising the steps of

(a) entering the exposed devices into the developer bath and removing the devices after the desired dwell time
(b) correcting the electrical conductivity of the partially exhausted developer bath by adding a replenisher to the developer, and optionally
(c) repeating step (b) at least once

wherein the replenisher is obtainable by the above described method.

[0019]   The present invention deals with the problem of different behavior of electrical conductivity of a developer and its activity, especially the case that the electrical conductivity does not decrease to the same extend as the activity decreases when developing a plurality of devices. The method provided herewith allows the developing of exposed radiation-sensitive devices like lithographic printing plates with constant activity of the developer without the need of a computer controlled system. According to the present invention a partially exhausted alkaline developer is refreshed by the addition of a strong alkaline replenisher which comprises an agent capable of suppressing the electrical conductivity of the developer to some extend.

[0020]   According to the method of the present invention the behaviour of the activity and the electrical conductivity

3

of the developer versus unit throughput of device to be processed are determined. Unit throughput can for instance be square meter throughput or a number of devices of a certain size.

[0021] The activity of the developer refers to the alkalinity of the developer, which is usually determined by titration with HCl (for instance 0.5 N HCl).

[0022] From the correlation of activity and unit throughput one can calculate the amount of hydroxide ions per unit throughput necessary for keeping the activity constant. In case of lithographic printing plates the replenisher used for adding the needed amount of hydroxide ions preferably contains a hydroxide ion source selected from at least one compound selected from alkali metal hydroxides, alkali metal silicates, water glass, and alkali metal phosphates in such a concentration that about 25 to 200 mL, preferably 30 to 60 mL, of replenisher per m^2 of developed printing plate are sufficient for replacing the consumed OH⁻ in the developer. An amount lower than about 25 mL is not preferred since per m^2 of developed printing plate about 25 mL of developer are removed from the developing bath with the plate and the content of the developer bath should be kept approximately constant. An amount higher than about 100 mL is not preferred from an economical point of view since by doing so the amount of waste drastically increases.

[0023] In a preferred embodiment a constant amount of replenisher is added after every processed device. In a continuous developing process it is, however, also possible to add a different amount of replenisher after a different amount of processed device, as long as the amount of replenisher is for instance doubled if the amount of throughput (e.g. in m^2) is doubled.

[0024] The starting developer can but does not necessarily contain the suppressing agent. According to one embodiment the process of the present invention the starting developer also contains the electrical conductivity suppressing agent used in the replenisher, however, in a much lower concentration, for example 0.15 to 0.5 times of the concentration used in the replenisher, more preferred 0.2 to 0.3 times.

[0025] The electrical conductivity suppressing agent is a polar organic substance which is water soluble. Furthermore, it has to be inert, i.e. it does neither react with the other components of the replenisher or the developer nor react with or attack the radiation-sensitive layer of the device to be developed.

[0026] The electrical conductivity suppressing agent is preferably selected from glycerol, diols, mono- or diethers of diols, esters of diol monoethers, ketones substituted with at least one hydroxy group and/or alkoxy group, ethers, alkanol amines, alkanols and amides of organic acids.

[0027] Examples for suitable diols are for instance those represented by the following formula

$$\begin{array}{cc} OH & OH \\ | & | \\ R^1\text{-}CH\text{-}(CH_2)_x\text{-}CH\text{-}R^2 \end{array}$$
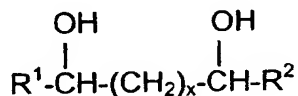
[0028] Wherein x is 0 or an integer from 1 to 4 and R^1 and R^2 are each independently selected from hydrogen and C_1-C_3 alkyl. Especially preferred diols are ethylene glycol, hexylene glycol, hexane-1,6-diol, propane-1,3-diol and butane-1,4-diol.

[0029] Also suitable are mono- and diethers obtained from said diols and C_1-C_4 alkanols, like methoxy propanol and 1,2-dimethoxy ethan.

Such monoethers can additionally be esterified with an organic acid selected from formic and acetic acid.

[0030] Further suitable electrical conductivity suppressing agents are ketones substituted with at least one hydroxy group and/or alkoxy group like methoxyacetone and diacetone alcohol.

[0031] Ethers of the following formula are further examples of suitable electrical conductivity suppressing agents

$$R^3\text{-}O\text{-}R^4$$
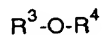
wherein R^3 and R^4 are independently selected from alkyl groups having 1 to 4 carbon atoms.

[0032] Especially preferred are cyclic ethers, i.e. ethers where R^3 and R^4 together with the oxygen atom to which they are bonded form a 5 or 6 membered ring.

Preferably the ether is 1,4-dioxane, methyl butyl ether and tetrahydrofuran.

[0033] Examples of suitable alkanol amines are those represented by the following formula:

$$R^5{}_m\text{-}N\text{-}(\text{-}CH_2\text{-}CH\ R^6\text{-}OH)_n$$
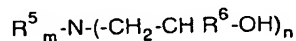
wherein m is 0, 1 or 2, n is 1, 2 or 3, m+n=3, R^5 and R^6 are each independently H or C_1-C_2 alkyl.

Especially preferred are monoethanol amine, diethanolamine, mono (isopropanol) amine and tri(isopropanol)amine.

[0034] C_3-C_6-Alkanols can also be used. The alkyl moiety can be a straight chain or branched chain alkyl as well as a cycloalkyl. The hydroxy group may be bonded to a terminal carbon atom or may be bonded to a carbon atom within the carbon skeleton. Suitable examples are butanol-2 and isopropanol.

[0035] Furthermore, the C_3-C_6 alkanols may further contain an amino group $-NH_2$; examples thereof are ethanolamine and propanolamine.

[0036] In addition, amides of organic acids represented by the following formula can be used as electrical conductivity suppressing agent in the method of the present invention

$$R^7\text{-}C\!=\!O$$
$$|$$
$$NR^8R^9$$
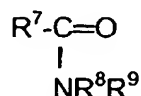
wherein R^7 is selected from hydrogen, methyl or ethyl, R^8 and R^9 are each independently H or C_1-C_3 alkyl.

[0037] From the above-mentioned suppressing agents the following are especially preferred: ethylene glycol, hexane-1,6-diol.

[0038] The kind of suppressing agent useful for a certain developing process depends - beside other factors - from the kind of radiation-sensitive layer on the device to be developed since it is important that the suppressing agent does not attack said layer.

The amount of the electrical conductivity suppressing agent in the replenisher depends on the developer composition as well as the kind of radiation sensitive layer to be developed. In most cases the amount is suitably in the range of about 2 to about 15 wt.-% based on the total replenisher composition, more preferably from about 4 to about 11 wt.-%.
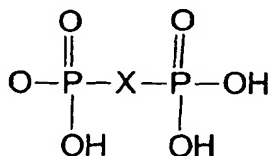
[0039] Besides the electrical conductivity suppressing agent the replenisher comprises water and at least one component selected from alkali metal hydroxides (like lithium hydroxide, sodium hydroxide, potassium hydroxide and ammonium hydroxide), alkali metal metasilicates, water glass, alkali metal phosphates, alkali metal carbonates and hydrogen carbonates, or alkali metal borates in order to provide sufficient alkalinity. In order to be able to increase the alkalinity of a partially exhausted developer it is necessary that the amount of the hydroxide, metasilicate, water glass, phosphates, carbonates, hydrogen carbonates and/or borates in the replenisher is distinctly higher than in the developer; preferably the amount in the replenisher is 1.2 to 1.6 times as high as in the developer.

[0040] It is preferred that the alkalinity of the replenisher is 1.2 to 1.6 times as high as that of the original developer; furthermore, the electrical conductivity of the replenisher is preferably also higher than that of the original developer (e.g 1.1 to 1.5 times as high as that of the original developer).
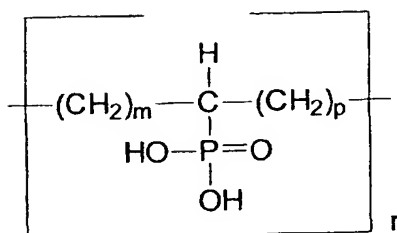
[0041] Optionally the replenisher further comprises at least one member selected from surfactants, etch inhibitors, antifoaming agents, chelating agents and biocides.

[0042] Examples of chelating agents include polyphosphoric acids and their sodium, potassium and ammonium salts; aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraamine-hexaacetic acid, hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, 1,2-diaminocyclohexanetetraacetic acid, 1,3-diamino-2-propanoltetraacetic acid, etc., and their sodium, potassium and ammonium salts; aminotri(methylene-phosphonic acid), ethylenediaminetetra(methylenephosphonic acid), diethylenetri-aminepenta(methylenephosphonic acid), triethylenetetraminehexa(methylene-phosphonic acid), hydroxyethylethylenediaminetri(methylenephosphonic acid) and 1-hydroxyethane-1,1-diphosphonic acid, and their sodium, potassium and ammonium salts.
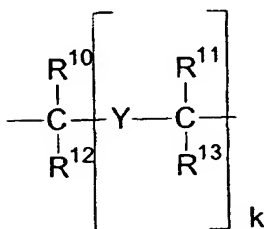
[0043] Preferred chelating agents which simultaneously also act as etch inhibitors are phoshonic acid derivatives like those represented by the formula

$$\begin{array}{ccc} O & & O \\ \| & & \| \\ O\!-\!P\!-\!X\!-\!P\!-\!OH \\ | & & | \\ OH & & OH \end{array} \qquad\qquad I$$

in which X is C_2-C_6 alkylene or

5

$$-\left[(CH_2)_m - \underset{\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}}{\overset{H}{|}} - (CH_2)_p\right]_r$$

10

or

15

20

$$-\left[\underset{\underset{R^{12}}{|}}{\overset{\overset{R^{10}}{|}}{C}} - Y - \underset{\underset{R^{13}}{|}}{\overset{\overset{R^{11}}{|}}{C}}\right]_k$$

25

[0044] in which k = 0 or 1; m = 1, 2, 3; p = 1, 2, 3; r is an integer from 10-20; R^{10} and R^{11} are each independently H or C_1-C_4 alkyl; R^{12} and R^{13} are each independently H, OH or C_1-C_4 alkoxy; and Y is -R^9N-$(CH_2)_n$-$(NR^8)_q$-, in which q = 0 or 1, n is an integer from 0 to 8 and R^8 and R^9 are each independently H, C_1-C_4 alkyl or -CH_2-P(O)(OH)$_2$.

[0045] Especially preferred are hydroxyethane diphosphonic acid, aminotri(methylene-phosphonic acid), hexamethylene diaminotetra(methylenephosphonic acid), sodium salts thereof, and mixtures thereof.

[0046] The amount of the chelating agent or mixture of the chelating agents is from 0 to 5 wt.-% based on the total composition of the replenisher.

[0047] Examples of the surfactant which can be used include nonionic surfactants, such as polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene polystyryl phenyl ethers, polyoxyethylenepolyoxypropylene alkyl ethers, glycerin fatty acid partial esters, sorbitan fatty acid partial esters, pentaerythritol fatty acid partial esters, propylene glycol monofatty acid esters, cane sugar fatty acid partial esters, polyoxyethylenesorbitan fatty acid partial esters, polyoxyethylenesorbitol fatty acid partial esters, polyethylene glycol fatty acid esters, polyglycerin fatty acid partial esters, polyoxyethylenized castor oils, polyoxyethylene-glycerin fatty acid partial esters, fatty acid diethanolamides, N,N-bis-2-hydroxyalkylamines, polyoxyethylene alkylamines, triethanolamine fatty acid esters, and trialkylamine oxides; anionic surfactants, such as fatty acid salts, abietic acid salts, hydroxyalkanesulfonic acid salts, alkanesulfonic acid salts, dialkylsulfosuccinic acid esters, straight-chain alkylbenzenesulfonic acid salts, branched alkylbenzenesulfonic acid salts, alkylnaphthalenesulfonic acid salts, alkylphenoxypolyoxyethylenepropylsulfonic acid salts, polyoxyethylene alkyl sulfophenyl ethers, N-methyl-N-oleyltaurin sodium salt, N-alkylsulfosuccinic acid monoamide disodium salts, petroleum sulfonic acid salts, sulfated beef-tallow oil, sulfates of fatty acid alkyl esters, alkylsulfuric acid esters, polyoxyethylene alkyl ether sulfuric acid esters, fatty acid monoglyceride sulfuric acid esters, polyoxyethylene alkyl phenyl ether sulfuric acid esters, polyoxyethylene styryl phenyl ether sulfuric acid esters, alkylphosphoric acid esters, polyoxyethylene alkyl ether phosphoric acid esters, polyoxyethylene alkyl phenyl ether phosphoric acid esters, partially saponified styrene/maleic anhydride copolymers, partially saponified olefin/maleic anhydride copolymers, and formaldehyde condensates of naphthalenesulfonates; cationic surfactants such as alkylamine salts, quaternary ammonium salts, polyoxyethylene alkylamine salts, and polyethylene polyamine derivatives, and amphoteric surfactants, such as carboxybetaines, aminocarboxylic acids, sulfobetaines, aminosulfuric acid esters, and imidazolines. The polyoxyethylene moiety present in some of the above-cited surfactants can be replaced by a polyoxypropylene, polyoxybutylene or another polyoxyalkylene moiety, and the resulting surfactants also can be included.

[0048] Further suitable surfactants are fluorinated surfactants in which a perfluoroalkyl group is present. Examples of such fluorinated surfactants include anionic ones, such as perfluoroalkylcarboxylic acid salts, perfluoroalkylsulfonic acid salts, perfluoroalkylphosphoric acid esters, etc.; amphoteric ones, such as perfluoroalkylbetaines, etc.; cationic ones, such as perfluoroalkyltrimethylammonium salts, etc.; and nonionic ones, such as perfluoroalkylamine oxides,

perfluoroalkylethylene oxide adducts, oligomers containing perfluoroalkyl and hydrophilic groups, oligomers containing perfluoroalkyl and lipophilic groups, oligomers containing perfluoroalkyl, hydrophilic and lipophilic groups, and urethanes containing perfluoroalkyl and lipophilic groups.

[0049] Preferred surfactants are sulfonic acid salts, sulfuric acid esters and compounds containing perfluoroalkyl groups.

[0050] The surfactant can be used alone or as a mixture of two or more thereof. The concentration of such a surfactant in the replenisher is generally from 0 to 10% by weight, preferably from 0.01 to 5% by weight.

[0051] Further, the replenisher can further contain one or more antifoaming agent if desired. Suitable antifoaming agents are for instance polydimethylsiloxanes or their copolymers. They are used in an amount of 0 to 1 wt.-% based on the total replenisher, more preferably of 0.01 to 0.5 wt.-%.

[0052] Examples of suitable etch inhibitors are for instance

$$R^{14}O(CH_2-CH-O)_s-R^{16}$$
$$\underset{R^{15}}{|} \qquad\qquad II$$
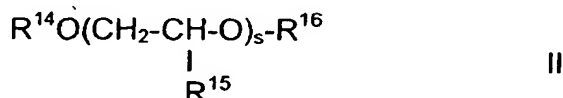
[0053] In which R^{14} is hydrogen or C_1-C_4 alkyl; R^{15} is hydrogen, methyl or ethyl; R^{16} is hydrogen or CH_2COOH; and s is an integer from 10 to 20.
They are used in an amount of 0 to 3 wt.-% based on the total weight of the replenisher composition, preferably 0.001 to 0.6 wt.-%.

[0054] Further suitable etch inhibitors are alkali metal phosphates and polyphosphates, and phosphonates.

[0055] The method of the present invention is especially suitable for developing positive working thermal plates comprising a radiation-sensitive layer which comprises

(a) at least one polymeric substance which is a phenolic resin soluble in an aqueous developer, is,
(b) at least one compound which reduces the developer solubility of the polymeric substance and is selected from imidazolium compounds, quinolinium compounds, benzothiazolium compounds and pyridinium compounds with quinolinium compounds being preferred and
(c) at least one compound which is capable of absorbing radiation and converting it to heat and is selected from one of the following classes: squarylium, merocyanine, indolizine, pyrylium and metal dithioline.

[0056] Such printing plates are described in EP-B-0 825 927.

[0057] In an especially preferred embodiment of the invention a replenisher is used which comprises

(a) at least one of alkali metal hydroxide and water glass,
(b) at least one phosphonic acid derivative selected from hydroxyethanediphosphonic acid, aminotri(methylenephosphonic acid), hexamethylenediaminotetra-(methylenephosphonic acid), sodium salts thereof, and mixtures thereof,
(c) at least one polyglycol derivative selected from polypropylene glycol ether, polyethylene glycol ether, polybutylene glycol ether, derivatives thereof, and mixtures thereof, and
(d) 8-15 wt.-% based on the total weight of the replenisher composition of a electrical conductivity suppressing agent selected from ethylene glycol and hexane-1,6-diol, and diacetone alcohol.

[0058] Any commonly used developing equipment can be used for carrying our the process according to the present invention.

[0059] The invention is now described in more details by the examples below

Example 1

Preparation of replenisher 1

[0060] A replenisher was prepared from the following components under stirring:

69.7 kg	water
19.1 kg	potassium hydroxide solution 45 wt.-% in water

7

(continued)

2.1 kg	phosphoric acid 85 wt.-% in water
6.1 kg	potassium waterglass 42/43 degrees Be in water
13 kg	ethylene glycol
0.21 kg	REWOTERIC® AM-V (wetting agent available from Witco)
0.21 kg	Sequion 10 Na (sodium salt of hydroxyethane diphosphonic acid)
0.24 kg	Synperonic T 304 (ICI Corp.)

and the mixture was subsequently filtered. It was stored in a closed container prior to use.

Example 2

Preparation of replenisher 2

[0061]   A replenisher was prepared from the following components under stirring:

74 kg	water
11.0 kg	sodium hydroxide solution 50 wt.-% in water
2.0 kg	phosphoric acid 85 wt.-% in water
8.6 kg	sodium waterglass 37/40 degrees Be in water
3.7 kg	hexane-1,6-diol
0.18 kg	Trilon® B (tetrasodium salt of EDTA, available from BASF)
0.14 kg	Synperonic T 304

and the mixture was subsequently filtered. It was stored in a closed container prior to use.

Reference Example 1

Preparation of developer 1:

[0062]   A developer was prepared from the following components under stirring:

40.9 kg	water
5.8 kg	potassium hydroxide solution 45 wt.-% in water
1.1 kg	phosphoric acid 85 wt.-% in water
3.2 kg	potassium waterglass 42/43 degrees Be in water
1.5kg	glycerol
0.1 kg	REWOTERIC® AM-V
0.1 kg	Sequion 10 Na
0.12 kg	Synperonic T 304

and the mixture was subsequently filtered. It was stored in a closed container prior to use.

Reference Example 2

Preparation of developer 2:

[0063]   A developer was prepared from the following components under stirring:

41.3kg	water
3.8 kg	sodium hydroxide solution 50 wt.-% in water
1.1 kg	phosphoric acid 85 wt.-% in water
4.8 kg	sodium waterglass 37/40 degrees Be in water

8

(continued)

0.9 kg	hexane-1,6-diol
0.1 kg	Trilon B
0.08 kg	Synperonic T 304

and the mixture was subsequently filtered. It was stored in a closed container prior to use.

Reference Example 3

Preparation of developer 3:

[0064]   A developer was prepared which differed from developer 1 in that no glycerol was present and 42.4 kg water were used instead of 40.9 kg.

Comparative Example 1

Prepararation of Comparative replenisher 1:

[0065]   A replenisher was prepared from the following components under stirring:

72.3 kg	water
19.1 kg	potassium hydroxide solution 45 wt.-% in water
2.1 kg	phosphoric acid 85 wt.-% in water
6.1 kg	potassium waterglass 42/43 degrees Be in water
0.21 kg	REWOTERIC® AM-V
0.21 kg	Sequion 10 Na
0.24 kg	Synperonic T 304

and the mixture was subsequently filtered. It was stored in a closed container prior to use.

Comparative Example 2

Prepararation of Comparative replenisher 2:

[0066]   A replenisher was prepared which differed from replenisher 1 in that no ethylene glycol was present and 82.7 kg water were used instead of 69.7 kg.

Example 3

Developing of positive-working thermal plate

[0067]   The positive-working printing plate Electra® used in the following examples is available from Kodak Polychrome Graphics LLC. Electra® plates were cut to a size of 515 x 790 mm and exposed in the IR-exposure unit Trendsetter 3244 (from Creo/Heidelberg) using an energy of 10 W and a rotational speed of the drum of 180 rpm. The Kodak Professional Colorflow Strip (available from Eastman Kodak), which contains different elements for evaluating the quality of the copies was used for evaluation.

[0068]   A commercially available processor (Sprinter; Kodak Polychrome Graphics LLC), equipped with an immersion type developing bath, a section for rinsing with water, and a gumming and drying section, was used to develop the imagewise exposed plates. The processor was filled with 20L of the appropriate developer. Separately, a container for the replenisher was attached from which a predetermined amount of replenisher per square meter of developed plate was added to the developing bath via a pump.

[0069]   The following other processor parameters were kept constant in all tests:

| temperature of the developing bath | (23±1)°C |
| dwell time in the developer | 45 sec |

9

[0070] The electrical conductivity of the developing bath was monitored by a separately mounted electrical conductivity measuring unit of the type Conductivity Monitor (Unigraph). To determine the activity (i.e. the alkali content) 10 mL of the developer were removed from the developing bath, 90 mL deionized water were added, and titration was carried out with 0.5 N HCl (Titrino DMS 716. Metrohm). The number of mL used to reach the first equivalence point is referred to as alkali value.

[0071] To evaluate the copies obtained after development, the following criteria were examined:

[0072] Reproduction of the 1 and 2 pixel elements, optical density (OD) of the checkerboard dots of the pixel elements (measured with the apparatus D 19C/D 196 from Gretag/Macbeth).

Stability and load tests

[0073] Electra® plates exposed in the manner described above were developed one after another at a rate of 33 plates per day for 30 days (plus 5 weekend interruptions) in the Sprinter processor. The quality of the resulting copies was evaluated in terms of the criteria given above. At a throughput of 2 m^2/L the electrical conductivity was measured as well as the activity (by titration with 0.5 N HCl).

[0074] The results for replenisher 1 and developer 1 are listed in Table 1 below. The titration and electrical conductivity data show that the electrical conductivity as well as the activity of the developer can be kept constant during the long testing period by the addition of replenisher in the amount of 50 mL per m^2 of developed plate. This also becomes apparent in the almost constant values for the copy parameters after the development of 400 m^2 dots of 1 x 1 pixel elements were open independently from the throughput.

[0075] During the test period of 12 L of overflow of used developer was collected, which corresponds to about 30 mL/m^2 of processed printing plates. No formation of foam or precipitation was observed during the testing period. After the test was completed, the processor could be easily cleaned by rinsing with water, and no residue remained.

[0076] Neither ink acceptance nor toning problems occurred in printing tests of plates after different throughputs.

[0077] The procedure was repeated with Electra® plates and developer 2 and replenisher 2. It was found that by adding 49 mL of replenisher 2, the activity of the developer could be kept constant until the end of the testing at 18 m^2/L (electrical conductivity: 52.6 mS/cm; titration: 7.8 mL). Also, the copy parameters of OD = 95 for 95% dot screen and OD = 49 for 59% dot screen in the beginning only slightly changed to OD = 96 and OD = 51, respectively, after a plate throughput of 18 m^2/L. Plates developed with such a developing system showed no problems in ink acceptance or toning during the printing test at the print proof and upon restarting.

Table 1

Throughput (m^2/L)	Replenisher (mL/m^2)	Optical Density (95% dot)	Optical Density (50% dot)	Electrical conductivity (mS/cm)	Titration (mL 0.5 N HCl)
0		95	51	72.9	8.9
2	50	96	50	72.7	8.8
4	50	95	51	72.6	8.5
6	50	96	50	72.4	8.5
8	50	95	50	72.8	8.6
10	50	95	51	72.9	8.7
12	50	96	51	72.5	8.4
14	50	95	50	72.8	8.5
16	50	95	51	72.6	8.4
18	50	96	51	72.4	8.6
20	50	96	50	72.5	8.4

Example 4

Influence of organic compounds on electrical conductivity of replenisher solutions

[0078] A replenisher solution was prepared from the following components under stirring:

7.0 kg	water
2.0 kg	potassium hydroxide solution 45 wt.-% in water
0.2 kg	phosphoric acid 85 wt.-% in water
0.6 kg	potassium waterglass 42/43 degrees Be in water
0.02 kg	REWOTERIC® AM-V
0.02 kg	Sequion 10 Na
0.02 kg	Synperonic T 304

[0079] The electrical conductivity of this solution was monitored by a electrical conductivity measuring unit of the type Conductivity Monitor (Unigraph). The electrical conductivity of this solution was 180 mS/cm. By addition of definitive amounts of compounds listed in Table 2 several solutions, containing different wt.-% of these compounds, were prepared, and their electrical conductivity was measured by the same way, The results are given in Table 2. It is shown that all used polar organic compounds depress the electrical conductivity of the replenisher solution, however, to a different extent.

Table 2

Added Amount (wt.-%)	Water	Ethylene glycol	Iso-propanol	Dimethyl formamid	Hexylene glycol	Diethylene glycol	Phenyl glycol
5	174.0	144.0	145.2	146.6	146.9	144.6	162.0
10	165.8	121.4	119.6	122.4	119.2	121.1	147.6
15	158.5	103.2	100.3	98.4	96.8	99.3	131.2
20	151.9	90.7	88.6	78.8	83.6	80.6	124.6
25	144.7	80.3	74.5	59.5	69.1	65.8	109.3
30	136.1	71.6	69.1	44.9	56.5	52.7	96.4

Table 2 (continued)

Added Amount (wt.-%)	Hexane diol-1.6	Mono-ethanol amine	2-Methoxy ethyl acetate	Methoxy Acetone	1.2-Di-methoxy ethane	1.4-Dioxane	Poly glycol 2000	Glycerol
5	165.1	143.5	109.2	144.5	143.8	167.7	146.4	145.3
10	133.6	114.3	71.4	120.4	125.2	139.7	128.0	125.5
15	114.1	91.6	61.8	99.9	90.5	113.5	107.5	111.6
20	94.9	72.9	*	76.1	68.4	91.1	*	95.1
25	79.8	53.6	*	58.2	40.6	72.4	*	84.7
30	65.0	41.7	*	56.8	23.9	50.4	*	75.9

* Added amount not soluble in the replenisher

Comparative Example 3

Stability and load tests with compositions of Comparative Example 1

[0080] Electra® plates were developed in the same manner as described above in the developing processor with the developer 3 and the replenisher listed in Comparative Example 1. Compared to replenisher solution 1, this replen-

isher contains no conductivity suppressing agent. The procedures to determine the plate quality and developer activity are identical with these of the above given load tests.

[0081] These tests provide the following results:

[0082] At a replenishment rate of 40 mL/m², the electrical conductivity parameter remained constant. The activity of the developer, however, decreased with the number of loaded plates leading to an unacceptable plate quality, see Table 3 below.

Table 3

Throughput (m²/L)	Replenisher (mL/m²)	Optical Density (95% dot)	Optical Density (50% dot)	Electrical conductivity (mS/cm)	Titration (mL 0.5 N HCl)
0		96	49	89.0	8.9
2	40	96	50	88.9	8.7
4	40	95	51	89.2	8.5
6	40	96	52	89.3	8.4
8	40	97	50	89.2	8.2
10	40	96	52	89.1	8.0
12	40	97	51	89.2	7.9
14	40	97	52	89.3	7.7
16	40	98	52	89.1	7.5
18	40	98	53	89.3	7.4
20	40	99	53	89.2	7.2

[0083] At a replenishment rate of 50 mL/m², the activity of the developer remained constant. The electrical conductivity parameter, however, increased with the number of loaded plates. Due to the constant developer activity the plate quality parameters also remain constant, see Table 4 below. As is apparent from Tables 3 and 4 it is not possible to infer the activity of the developer from the measurement of the electrical conductivity.

Table 4

Throughput (m²/L)	Replenisher (mL/m²)	Optical Density (95% dot)	Optical Density (50% dot)	Electrical conductivity (mS/cm)	Titration (mL 0.5 N HCl)
0		95	48	89.1	8.8
2	50	96	47	90.7	8.6
4	50	95	47	92.0	8.7
6	50	95	49	93.1	8.6
8	50	96	47	94.6	8.5
10	50	96	48	95.5	8.4
12	50	95	47	96.9	8.6
14	50	95	49	98.3	8.5
16	50	96	47	99.5	8.4
18	50	95	49	101.2	8.5
20	50	96	47	102.9	8.6

[0084] The above tests clearly show that a determination of the developer activity by means of electrical conductivity is only possible if a sufficient amount of electrical conductivity suppressing agent is present in the replenisher solution.

Comparative Example 4

[0085]   Electra® plates were developed in the same manner as described above in Example 3 by using developer 3.

[0086]   At a replenishment rate of 50 mL/m² of the comparative replenisher 2 the measured electrical conductivity continually increased while the activity of the developer bath remained constant.

Example 5

[0087]   Electra® plates were developed in the same manner as described above in Example 3 by using developer 3.

[0088]   At a replenishment rate of 50 mL/m² of the replenisher 1 the measured electrical conductivity as well as the activity of the developer bath remained constant.

Example 6

[0089]   Electra® plates were developed in the same manner as described above in Example 3 by using developer 3.

[0090]   At a replenishment rate of 50 mL/m² of the replenisher 2 the measured electrical conductivity as well as the activity of the developer bath remained constant.

Claims

1. A method for the production of a replenisher composition useful for refreshing a partially exhausted developer having a lower activity than it appears from the electrical conductivity, comprising the steps:

    (a) measuring the activity and electrical conductivity versus unit throughput of device to be processed while using the desired developer
    (b) determining the amount of hydroxide ions per unit throughput necessary for achieving the original activity
    (c) for the case that the electrical conductivity per unit throughput does not decrease as it should decrease due to consumption of OH^-, determining the amount of a electrical conductivity suppressing agent necessary for keeping the electrical conductivity constant, wherein the electrical conductivity suppressing agent is water soluble, does not react with the other components of the replenisher and developer and does not react with or attack the radiation-sensitive layer of the device to be developed
    (d) mixing water and the hydroxide ion source with the electrical conductivity suppressing agent and optional further components.

2. The method according to claim 1, wherein the replenisher comprises besides the electrical conductivity suppressing agent:

    at least one component selected from alkali metal hydroxides, alkali metal metasilicate, water glass and alkali metal phosphates as hydroxide ion source
    and optionally at least one member selected from phosphonic acids and
    derivatives thereof, surfactants, polyglycols, anti-foaming agents, chelating agents and biocides.

3. The method according to claim 1 or 2, wherein the electrical conductivity suppressing agent is selected from diols, mono- or diethers of diols, esters of diol monoethers, ketones substituted with at least one hydroxy group or alkoxy group, ethers, alkanol amines, alkanols and amides of organic acids.

4. The method according to claim 3, wherein the electrical conductivity suppressing agent is selected from ethylene glycol, hexylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, hexane-1,6-diol, isopropanol, monoethanol amine, methoxy acetone, 1,2-dimethoxy ethane, 1,4-dioxane, 2-methoxy ethyl acetate, dimethyl formamide.

5. The method according to any one of claims 1 to 4, wherein the amount of electrical conductivity suppressing agent in the replenisher is in the range from about 2 to about 15 wt.-% based on the total composition.

6. Method according to any one of claims 1 to 5, wherein the alkalinity of the replenisher is 1.2 to 1.6 times as high as that of the original developer.

7. Method according to any one of claims 1 to 6, wherein the electrical conductivity of the replenisher is 1.1 to 1.5 times as high as that of the original developer.

8. A method for developing radiation-sensitive imagewise exposed devices by using an alkaline developer showing electrical conductivity, comprising the steps of

(a) entering the exposed devices into the developer bath and removing the devices after the desired dwell time
(b) correcting the activity of the partially exhausted developer bath by adding a replenisher to the developer, and optionally
(c) repeating step (b) at least once

wherein the replenisher is obtainable by the method of any of claims 1 to 10.

9. Method according to claim 8, wherein a constant amount of replenisher is added to the partially exhausted developer per unit of processed device.

10. Method according to claim 8 or 9, wherein the device to be processed is an imagewise exposed lithographic printing plate precursor.

11. Method according to claim 10, wherein the alkalinity and the amount of the electrical conductivity suppressing agent in the replenisher is such that the alkalinity and the conductivtiy of the developer can be kept constant by adding 30 to 60 mL replenisher per unit of processed lithographic printing plate precursor to the developer.

12. Replenisher composition comprising

(a) at least one component selected from alkali metal hydroxide, alkali metal metasilicate, water glass and alkali metal phosphates
(b) at least one electrical conductivity suppressing agent which is soluble in water, does not react with the other components of the replenisher and developer, does not react with or attack the radiation-sensitive layer of the device to be developed
and optionally
(c) at least one member selected from phosphonic acids and derivatives thereof, surfactants, polyglycols, antifoaming agents, chelating agents and biocides.

13. Composition according to claim 12, having a pH of 10 to 14.

14. Composition according to claim 12 or 13, wherein the electrical conductivity suppressing agent is selected from diols, mono- or diethers of diols, esters of diol monoethers, ketones substituted with at least one hydroxy group or alkoxy group, ethers, alkanol amines, alkanols and amides of organic acids.

15. Composition according to claim 14, wherein the electrical conductivity suppressing agent is selected from the group consisting of ethylene glycol, hexylene glycol, diethylene glycol, polyethylene glycol, polypropylene glycol, hexane-1,6-diol, isopropanol, monoethanol amine, methoxy acetone, 1,2-dimethoxy ethane, 1,4-dioxane, 2-methoxy ethyl acetate, dimethyl formamide.

16. Composition according to any one of claims 12 to 15, wherein the amount of electrical conductivity suppressing agent is in the range from 2 to 15 wt.-% based on the total composition.

17. Use of a composition as defined in any of claims 12 to 16 for refreshing a partially exhausted developer.

18. Use of a replenisher obtained by the method of any of claims 1 to 7 for refreshing a partially exhausted developer.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 00 12 3444

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X,Y	EP 1 037 116 A (FUJI PHOTO FILM CO., LTD.) 20 September 2000 (2000-09-20) * page 9, line 43,44 * * page 10, line 12-23 * * page 29, line 40-53 * * page 31, line 37-52; claims 1,9,13 *	1-18	G03F7/30 G03F7/32
X,D	DE 44 11 176 A (FUJI PHOTO FILM CO., LTD.) 6 October 1994 (1994-10-06) * page 2, line 53-55 * * page 4, line 53 - page 5, line 8 * * page 5, line 18-35 * * page 16, line 49-54; claims 7-12 *	12-18	
X	EP 0 405 986 A (KONICA CORPORATION) 2 January 1991 (1991-01-02) * claims 1,9,12 *	12-18	
X	EP 0 716 347 A (FUJI PHOTO FILM CO., LTD.) 12 June 1996 (1996-06-12) * claims 1-3 *	12-18	
Y	EP 0 490 515 A (FUJI PHOTO FILM CO., LTD.) 17 June 1992 (1992-06-17) * claims 1,15,16 *	1-18	TECHNICAL FIELDS SEARCHED (Int.Cl.7) G03F
Y	DE 39 21 564 A (P. LÜTTGEN) 17 January 1991 (1991-01-17) * column 3, line 63 - column 5, line 61 *	1-11	
Y	US 5 853 963 A (SINGH ET AL.) 29 December 1998 (1998-12-29) * claim 6 *	1-11	
E	EP 1 081 554 A (KODAK POLYCHROME GRAPHICS COMPANY LTD.) 7 March 2001 (2001-03-07) * page 7, line 34 - line 53; examples 1-4 *	1-18	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	21 May 2001	Thiele, N

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 00 12 3444

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information

21-05-2001

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 1037116	A	20-09-2000	JP 2000267296 A JP 2000352826 A		29-09-2000 19-12-2000
DE 4411176	A	06-10-1994	JP 3086354 B JP 6282079 A GB 2276729 A,B		11-09-2000 07-10-1994 05-10-1994
EP 405986	A	02-01-1991	CA 2019632 A JP 3101735 A		29-12-1990 26-04-1991
EP 716347	A	12-06-1996	JP 8160631 A JP 8234447 A US 5837425 A		21-06-1996 13-09-1996 17-11-1998
EP 490515	A	17-06-1992	CA 2056302 A DE 69127958 D DE 69127958 T JP 5002271 A US 5480762 A		29-05-1992 20-11-1997 12-02-1998 08-01-1993 02-01-1996
DE 3921564	A	17-01-1991	NONE		
US 5853963	A	29-12-1998	NONE		
EP 1081554	A	07-03-2001	US 6143479 A		07-11-2000

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82